

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 May 2003 (08.05.2003)

PCT

(10) International Publication Number
WO 03/037948 A1

(51) International Patent Classification⁷: C08G 18/12,
C08F 283/00, C08G 18/76, 18/50

(74) Agent: SIMS, Norman, L.; The Dow Chemical Company,
Intellectual Property, P.O. Box 1967, Midland, MI 48641-
1967 (US).

(21) International Application Number: PCT/US02/33751

(22) International Filing Date: 22 October 2002 (22.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Date:
10/055,220 29 October 2001 (29.10.2001) US

(63) Related by continuation (CON) or continuation-in-part
(CIP) to earlier application:
US 10/055,220 (CIP)
Filed on 29 October 2001 (29.10.2001)

(71) Applicant (for all designated States except US): DOW
GLOBAL TECHNOLOGIES INC. [US/US]; Washing-
ton Street, 1790 Building, Midland, MI 48674 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): LEKOVIC, Huzeir
[BA/US]; 5920 Houghton, Troy, MI 48098 (US). BIL-
LOTTO, Frank, V. [US/US]; 903 High Street, Rochester,
MI 48307 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ,
DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, YU, ZA,
ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

D2

(54) Title: RIGID HYBRID POLYURETHANE FOAMS

(57) Abstract: Rigid polyurethane foams that can be produced at component volumes ratios of less than 4:1 are prepared from an isocyanate component that contains certain polyfunctional (meth)acrylate compounds. These isocyanate components are mixed with a polyol component to produce rigid foams. The foams are particularly suitable for foam-in-place applications, such as for reinforcing structural members of automobiles.



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component in the presence of (i) a blowing agent, (ii) at least one polyfunctional (meth)acrylate compound containing an average of at least 2 acrylate or methacrylate groups per molecule and a weight per acrylate or methacrylate group of 300 daltons or less and (iii) at least one catalyst for the reaction of a polyol or water with a polyisocyanate and, subjecting the mixture to conditions sufficient to cause the isocyanate component and polyol component to react and the polyfunctional (meth)acrylate compound to polymerize, thereby forming a rigid hybrid polyurethane foam having a bulk density of 45 pounds per cubic foot (720 kg/m^3) or less.

In a second aspect, this invention is a two-component reactive system for making a hybrid polyurethane foam, comprising

- (a) a isocyanate component that contains at least one polyisocyanate compound and at least one polyfunctional (meth)acrylate compound containing an average of at least 2 acrylate or methacrylate groups per molecule and a weight per acrylate or methacrylate group of 300 daltons or less; and
- (b) a polyol component that contains one or more polyols and an effective amount of a blowing agent;

wherein the system is further characterized by

- (i) a volume ratio of isocyanate component to polyol component of between 1:4 to 4:1,
- (ii) a ratio of isocyanate groups in the isocyanate component to isocyanate-reactive groups in the polyol component from 0.8:1 to 1.5:1 and
- (iii) at least one of the isocyanate component or the polyol component contains a catalyst for the reaction of an isocyanate with a polyol or water.

The process of this invention provides a method by which rigid hybrid polyurethane foam can be prepared at convenient mix ratios while still allowing the production good quality, rigid foam. The method and resulting foam is especially suitable for making foamed-in-place reinforcing and sound- or vibration-dampening foam, especially for automotive applications, as it is easily foamed in place where reinforcement is needed. Through the selection of appropriate catalysts, the reactive

trimethylolpropanetriacrylate, di(trimethylolpropane) tetracrylate (Sartomer 355), di(trimethylolpropane) tetramethacrylate and similar compounds.

The amount of polyfunctional (meth)acrylate compound that is used is selected in conjunction with the amounts of the other components so that the resulting foam is rigid and stable. In the preferred two-component method of making the foam, the amount of the polyfunctional (meth)acrylate compound is also selected in conjunction with the amounts of other components so the volume ratio of the isocyanate component to the polyol component is within the ranges described below. The precise amount that is required will depend on the relative equivalent weights of the isocyanate component and the polyols in the polyol component. However, these volume ratios are generally achieved when the polyfunctional (meth)acrylate compound constitutes from 1, preferably 3, more preferably 5, to 35, preferably to 30 percent of the total weight of the foam formulation. To obtain a stable, rigid foam, the polyfunctional (meth)acrylate compound preferably constitutes at least 15 percent of the total weight of the foam formulation. When, as preferred, the polyfunctional (meth)acrylate compound is incorporated into the isocyanate component, it will generally constitute from 10, preferably from 20, more preferably 25 to 60, preferably to 50, more preferably to 45 percent of the total weight of the isocyanate component.

The isocyanate component comprises one or more polyisocyanate compounds, and preferably contains the polyfunctional (meth)acrylate compound. Suitable polyisocyanate compounds include aromatic, aliphatic and cycloaliphatic polyisocyanates. Aromatic polyisocyanate compounds are generally preferred based on cost, availability and properties, although aliphatic polyisocyanates are sometimes preferred in instances where stability to light is important. Exemplary polyisocyanate compounds include, for example, m-phenylene diisocyanate, 2,4- and/or 2,6-toluene diisocyanate (TDI), the various isomers of diphenylmethanediisocyanate (MDI), hexamethylene-1,6-diisocyanate, tetra methylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate, hydrogenated MDI (H_{12} MDI), naphthylene-1,5-diisocyanate, methoxyphenyl-2,4-diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, 4,4',4''-triphenylmethane diisocyanate,

glycerine, trimethylolpropane, tertiary amine-containing polyols such as triethanolamine, triisopropanolamine, and ethylene oxide and/or propylene oxide adducts of ethylene diamine, toluene diamine and the like, polyether polyols, polyester polyols, and the like. Among the suitable polyether polyols are polymers of alkylene oxides such as ethylene oxide, propylene oxide and 1,2-butylene oxide or mixtures of such alkylene oxides. Preferred polyethers are polypropylene oxides or polymers of a mixture of propylene oxide and a small amount (up to 12 weight percent) of ethylene oxide. These preferred polyethers can be capped with up to 30 percent by weight ethylene oxide.

Polyester polyols are also suitable in making the prepolymer. These polyester polyols include reaction products of polyols, preferably diols, with polycarboxylic acids or their anhydrides or halides, preferably dicarboxylic acids or dicarboxylic acid anhydrides. The polycarboxylic acids, anhydrides or acid halides may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic and may be substituted, such as with halogen atoms. The polycarboxylic acids may be unsaturated. Examples of these polycarboxylic acids, anhydrides and acid halides include succinic acid, adipic acid, terephthalic acid, isophthalic acid, trimellitic acid, maleic acid, and fumaric acid, and their corresponding anhydrides and acid halides. The polyols used in making the polyester polyols preferably have an equivalent weight of 150 or less and include ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butane diol, 1,6-hexane diol, 1,8-octane diol, neopentyl glycol, cyclohexane dimethanol, 2-methyl-1,3-propane diol, glycerine, trimethylol propane, 1,2,6-hexane triol, 1,2,4-butane triol, trimethylolethane, pentaerythritol, quinitol, mannitol, sorbitol, methyl glycoside, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, dibutylene glycol and the like. Polycaprolactone polyols such as those sold by The Dow Chemical Company under the trade name "Tone" are also useful.

Preferred polyols for making the prepolymer are alkylene glycols, glycol ethers of up to 75 equivalent weight, glycerine, trimethylolpropane, triethanolamine, triisopropanolamine, and poly(propylene oxide) polyols of up to 200 equivalent weight.

An especially preferred prepolymer is made from an excess of an organic polyisocyanate compound, a hydroxy-functional acrylate or methacrylate, and a polyol. The equivalent ratio of the hydroxy-functional acrylate or methacrylate to polyol is

A catalyst may be and preferably is used in making the prepolymer.

Suitable catalysts include those described by U.S. Pat. No. 4,390,645. Representative catalysts include: (a) tertiary amines, such as trimethylamine, triethylamine, N-methylmorpholine, N-ethylmorpholine, N,N-dimethylbenzylamine, N,N-dimethylethanolamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N-dimethylpiperazine, 1,4-diazobicyclo-2,2,2-octane, bis(dimethylaminoethyl)ether, bis(2-dimethylaminoethyl) ether, morpholine, 4,4'-(oxydi-2,1-ethanediyl)bis and triethylenediamine;

(b) tertiary phosphines, such as trialkylphosphines and dialkylbenzylphosphines;

(c) chelates of various metals, such as those which can be obtained from acetylacetone, benzoylacetone, trifluoroacetyl acetone, ethyl acetoacetate and the like with metals such as Be, Mg, Zn, Cd, Pd, Ti, Zr, Sn, As, Bi, Cr, Mo, Mn, Fe, Co and Ni;

(d) acidic metal salts of strong acids, such as ferric chloride, stannic chloride, stannous chloride, antimony trichloride, bismuth nitrate and bismuth chloride;

(e) strong bases, such as alkali and alkaline earth metal hydroxides, alkoxides and phenoxides;

(f) alcoholates and phenolates of various metals, such as $Ti(OR)_4$, $Sn(OR)_4$ and $Al(OR)_3$, wherein R is alkyl or aryl, and the reaction products of the alcoholates with carboxylic acids, beta-diketones and 2-(N,N-dialkylamino)alcohols;

(g) salts of organic acids with a variety of metals, such as alkali metals, alkaline earth metals, Al, Sn, Pb, Mn, Co, Ni and Cu including, for example, sodium acetate, stannous octoate, stannous oleate, lead octoate, metallic driers, such as manganese and cobalt naphthenate; and

(h) organometallic derivatives of tetravalent tin, trivalent and pentavalent As, Sb and Bi and metal carbonyls of iron and cobalt.

Catalysts are typically used in small amounts. For example, the total amount of catalyst used in making the prepolymer composition may be 0.0015 to 5, preferably from 0.01 to 1 percent by weight.

The isocyanate component may contain a plasticizer. When the isocyanate component includes a prepolymer, the plasticizer may also be added after the prepolymer

700, more preferably to 500. The isocyanate functionality (exclusive of the polyfunctional (meth)acrylate compound and non-reactive materials such as plasticizers, surfactants and the like) is advantageously at least 2.0, preferably at least 2.5, to 4.0, preferably to 3.5, more preferably to 3.2 isocyanate groups/molecule on average.

The isocyanate component also preferably contains less than 25 percent, more preferably less than 12 percent, especially 10 percent by weight or less of monomeric diisocyanates. By "monomeric diisocyanates", it is meant isocyanate-containing species that (i) do not contain urethane, urea, biuret or carbodiimide linkages, (ii) have a molecular weight of 300 or less and (iii) which are not otherwise formed in the reaction of two or more isocyanate-containing compounds. Having such a low monomeric diisocyanate content substantially reduces the risks of polyisocyanate inhalation exposure, so costly engineering controls such as downdraft ventilation can be substantially reduced or potentially eliminated.

The polyol component includes one or more polyols. Suitable polyols are compounds having at least two isocyanate-reactive hydroxyl groups per molecule. Among the polyols that are suitable for use in the polyol component are those described above with respect to the isocyanate-terminated prepolymer. The polyol component will most typically include a blend of two or more different polyols.

The equivalent weight and functionality of the individual polyols can vary widely, provided the volume ratios and equivalent ratios discussed below are met. Although it is important in most rigid polyurethane foam formulations that the polyol(s) have a high average functionality and low equivalent weight, that is not necessarily the case in this invention, for reasons that are more fully explained below. The functionality (average number of isocyanate-reactive groups/molecule) of the individual polyols can range as low as 1.8 or as high as 8 or more, and the equivalent weight of the individual polyols can range from as low as 31 to as high as 3000 or more. These same values apply to the average functionality of all the polyols and amine-functional compounds (if present) in the polyol component (but exclusive of the polyfunctional (meth)acrylate compound, other non-isocyanate reactive materials, reactive catalysts as described below, and reactive blowing agents, if present).

particles may be, for example, polymers of a vinyl monomer (such as styrene, acrylonitrile or styrene-acrylonitrile particles), polyurea particles or polyurethane particles. Polymer or copolymer polyols containing from 2 to 50 percent or more by weight dispersed polymer particles are suitable. When used, this polymer or copolymer polyol may constitute up to 45 percent, preferably from 5 to 40 percent, of the weight of all isocyanate-reactive materials in the polyol component.

The polyether polyols described above may be made using production methods such that they contain reduced levels of terminal unsaturation (such as less than 0.04 meq/g, preferably from 0.005 to 0.035 meq/g). Such production methods include the use of low temperature, alkali metal-catalyst polymerizations, CsOH-catalyzed polymerizations, so-called double metal cyanide-catalyzed polymerizations, various acid-finishing techniques, and the like.

The polyol component may include at least a small amount of a tertiary amine-containing polyol and/or an amine-functional compound. The presence of these materials tends to increase the reactivity of the polyol component during the early stages of its reaction with the isocyanate component. This in turn helps the reaction mixture to build viscosity more quickly when first mixed and applied without unduly decreasing cream time, and thus reduces run-off or leakage.

Such tertiary amine-containing polyols include, for example, triisopropanol amine, triethanolamine and ethylene and/or propylene oxide adducts of ethylene diamine, toluene diamine or aminoethylpiperazine having a molecular weight of up to 3000, preferably up to 2000. When present, tertiary amine-containing polyols may constitute a minor or a major component of the polyol component. (In this invention, a "major" or "main" amount or a "major" or "main" component is one constituting at least 50 weight percent of the polyol component as a whole.) For example, the tertiary amine-containing polyol may constitute from 1 to 80 percent by weight of all polyols.

The amine-functional compound is a compound having at least two isocyanate-reactive groups, of which at least one is a primary or secondary amine group. Among these are monoethanolamine, diethanolamine, monoisopropanol amine, diisopropanol amine and the like, and aliphatic polyamines such as

are N,N,N-trimethyl-N-hydroxyethyl-bis (aminoethyl) ether (available from Huntsman Chemical under the trade name ZF-10) and dimethyl 1-2 (2-aminoethoxy) ethanol (available from Nitrol-Europe under the trade name NP-70), and those sold by Air Products under the trade names Dabco™ 8154 and Dabco™ T.

The amount of catalyst is selected to provide a desired reaction rate. The amount that is used will depend somewhat on the particular catalyst. Generally, the amounts described before with respect to the making of the prepolymer are suitable. However, when the preferred reactive amine catalysts are used, somewhat greater amounts can be used. For these reactive amine catalysts, the amount used preferably ranges from 1 to 15, more preferably from 2 to 13 percent of the total weight of the polyol component.

In order to promote the polymerization of the polyfunctional (meth)acrylate compound, the reaction is preferably conducted in the presence of a free radical initiator. This is generally incorporated into the component that does not contain the polyfunctional (meth)acrylate compound. These compounds are well known, and include hydrogen peroxide, various organic peroxides, peresters and percarbonates, the so-called "azo" type free radical initiators, various persulfates, and redox systems. Organic peroxides, peresters and percarbonates are preferred. Often, a promoter compound such as cobalt naphthenate is used in conjunction with these free radical initiator compounds. Particular free radical initiators are preferably selected so that they are active at the temperatures generated by the exothermic reaction between the isocyanate component and the various isocyanate-reactive materials in the polyol component. Suitable amounts are from 0.01 to 3 percent of the total weight of the foam formulation.

In addition, the polyol component and/or the prepolymer component can contain various auxiliary components as may be useful in making a rigid foam, such as surfactants, fillers, colorants, odor masks, flame retardants, biocides, antioxidants, UV stabilizers, antistatic agents, thixotropic agents and cell openers.

Suitable surfactants include commercially available polysiloxane/polyether copolymers such as Tegostab (trademark of Goldschmidt

blowing agents and catalysts when present) for form a polyurethane polymer, (2) the acrylate and/or methacrylate groups on the polyfunctional (meth)acrylate compound polymerize (together with acrylate and/or methacrylate groups that are present in the most preferred prepolymer component) and (3) gasses are generated so that the mixture cures for form a stable, rigid foam that is most preferably closed celled.

This is generally achieved by mixing the polyol and isocyanate components and allowing the reactants to react and form a foam. The components may be pre-heated if desired. Although this invention is not limited to any theory, it is believed that as the prepolymer reacts with the polyol component, the heat that is released causes (in conjunction with the free radical initiator, when used) the acrylate and/or methacrylate groups to polymerize, thus forming a cross-linked acrylate or methacrylate polymer dispersed within a polyurethane matrix. When the prepolymer is acrylate- or methacrylate functional as most preferred, this acrylate or methacrylate polymer is believed to become covalently bonded to the prepolymer molecules as well and thus are incorporated into the polyurethane polymer matrix. An advantage of the invention is that because of the low volume ratios of the polyol and isocyanate components, a variety of commonly available mixing and dispensing equipment can be used. In the applications of particular interest, the mixed isocyanate and polyol components are dispensed onto a part or assemblage where localized reinforcement, corrosion protection, sound insulation or vibration dampening is desired. The formulation then cures in place, generally without the further application of additional heat or energy for curing, although heating can be used if desired to speed and/or complete the cure. Alternately, the foam can be formed separately and then glued or otherwise attached to the structural member. It is usually not necessary to apply heat to effect a full expansion and cure, although this may be done if desired. Similarly, it is usually not necessary to post-cure the foam, although it may be desired in some cases.

The density of the product foam is no greater than 45 pounds/cubic foot (720 kg/m^3), and preferably is from 1 (16), more preferably from 2 (32), even more preferably from 4 (64) pcf (kg/m^3) to 30 (480), more preferably to 20 (320), even more preferably to 15 (240) pcf (kg/m^3). The foam is typically rigid and dimensionally stable, and preferably contains mainly closed cells.

The resulting plasticized prepolymer has a % NCO of 12.93 weight percent, an equivalent weight of 325 and an average functionality (exclusive of plasticizer) of 2.92 isocyanate groups/molecule.

C. Manufacture of Foam Example 1

An isocyanate component was prepared by blending 25.68 parts by weight of the prepolymer from A above with 15 parts of trimethylolpropane trimethacrylate (Sartomer™ SR 350, from Sartomer Corporation) and 0.5 parts t-butyl peroxide. The resulting blend was mixed with the polyol component from B above at a weight ratio of 41.18 to 26.18. Mixing was done at room temperature using a mechanical mixer. The mixed components were poured into an open container and allowed to cure at room temperature. The resulting foam was closed-cell and rigid. It has a density of 6.66 pounds per cubic foot (106.6 kg/m³).

D. Manufacture of foam example 2

An isocyanate component was prepared by blending 27.03 parts by weight of the prepolymer with 23.14 parts of Sartomer™ SR 350 and 0.38 parts t-butyl peroxide. The resulting blend was mixed with the polyol component from B above at a weight ratio of 50.55 to 23.57, under the conditions described in C above. The resulting foam was closed-cell and rigid, with a density of 7.44 pounds per cubic foot (119 kg/m³).

When insufficient amounts of the polyfunctional (meth)acrylate compound were used, and/or the polyfunctional (meth)acrylate does not polymerize sufficiently (due to, for example, insufficient quantities of catalyst or improper curing conditions), flexible, dimensionally unstable foams were made.

Examples 3-6

A. Preparation of Isocyanate-terminated prepolymer

A polyisocyanate-terminated prepolymer was made by mixing the following components together under a nitrogen atmosphere and heating at 55°C until a constant NCO content was obtained:

Component	Parts by Weight	Equivalent Weight	Functionality
Polyether polyol (Voranol™ NC 700, from Dow Chemical)	79.5	2777	3
Amine-terminated polyether	15.0	1000	2
Catalyst (SPI 847 from Specialty Products International)	2.5		Catalyst
Organotin Catalyst (UL-1, from Air Products)	0.25		Catalyst
Organosilicone Surfactant (Tegostab B-8404, Goldschmidt)	1	--	Surfactant
Water	2.0		Reactive blowing agent
Co Naphthenate	0.5		Promoter

The resulting polyol blend has an equivalent weight of 372.4.

C. Manufacture of Foam Example 3

An isocyanate component was prepared by blending 18.77 parts by weight of the isocyanate-terminated prepolymer from A above with 18.93 parts Sartomer 350 and 0.9 parts t-butyl peroxide. The isocyanate component was then mixed with 18.93 parts of the polyol component from B above, under the general conditions described in

CLAIMS

1. A method of making a rigid hybrid polyurethane foam, comprising mixing an isocyanate component with a polyol component in the presence of (i) a blowing agent, (ii) at least one polyfunctional (meth)acrylate compound containing an average of at least 2 acrylate or methacrylate groups per molecule and a weight per acrylate or methacrylate group of 300 daltons or less and (iii) at least one catalyst for the reaction of a polyol or water with a polyisocyanate and subjecting the mixture to conditions sufficient to cause the isocyanate component and polyol component to react and the polyfunctional (meth)acrylate compound to polymerize, thereby forming a rigid hybrid polyurethane foam having a bulk density of 45 pounds per cubic foot (720 kg/m^3) or less.

2. The method of Claim 1, wherein the polyfunctional (meth)acrylate compound contains an average of from 2.5 to 5 acrylate or methacrylate groups per molecule.

3. The method of Claim 1 or 2, wherein the polyfunctional (meth)acrylate compound is blended with the isocyanate component prior to mixing the isocyanate component with the polyol component.

4. The method of any of Claims 1-3, wherein the isocyanate component includes an isocyanate-terminated prepolymer having an isocyanate-equivalent weight of from 150 to 500 and an average functionality of 2.7 to 4.0.

5. The method of any of Claims 1-4 wherein the volume ratio of isocyanate component plus the polyfunctional (meth)acrylate compound to the polyol component is from 4:1 to 1:4.

6. The method of Claim 4 or 5 wherein the prepolymer is made by reacting a polymeric MDI having a free MDI content of from 10-25 percent by weight with a polyol.

7. The method of any of Claims 1-6, wherein the polyol component includes a polyol having an equivalent weight of 1000 to 3000 and a tertiary amine-containing polyol and/or an amine-functional compound.

14. The reactive system of any of Claims 11-13 wherein the volume ratio of isocyanate component to the polyol component is from 4:1 to 1:4.

15. The reactive system of any of Claims 13-14 wherein the prepolymer is made by reacting a polymeric MDI having a free MDI content of from 10-25 percent by weight with a polyol.

16. The reactive system of any of Claims 11-15, wherein the polyol component includes a polyol having an equivalent weight of 1000 to 3000 and a tertiary amine-containing polyol and/or an amine-functional compound.

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International Application No.

PCT/US 02/33751

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 594 366 A (TAYLOR GLENN A ET AL) 10 June 1986 (1986-06-10) claim 37</p> <p style="text-align: center;">-----</p>	1-16